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*Published in:*  
Impacts of Fuel Quality on Power Production

*Publication date:*  
2016

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Wang, G., Jensen, P. A., Wu, H., Jappe Frandsen, F., Sander, B., & Glarborg, P. (2016). K-capture by Al-Si based Additives in an Entrained Flow Reactor. In *Impacts of Fuel Quality on Power Production*

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# K-capture by Al-Si based Additives in an Entrained Flow Reactor

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A water slurry, consisting of KCl and Al-Si based additives (kaolin and coal fly ash) was fed into an entrained flow reactor (EFR) to study the K-capturing reaction of the additives at suspension-fired conditions. Solid products collected from the reactor were analysed with respect to total and water-soluble K content to quantify the extent of the K-capturing reaction. The results showed that under suspension-fired conditions (1100 °C-1450 °C), kaolin and coal fly ash can effectively capture gaseous KCl. When increasing the mass ratio of KCl to Al-Si additives in the reactants, the conversion of KCl to K-aluminosilicate decreased. When reaction temperature increased from 1100 °C to 1450 °C, the conversion of KCl does not change significantly, which differs from the trend observed in fixed-bed reactor.

**Keywords:** K-capture, biomass combustion, kaolin, coal ash

## 1. Introduction

Presently, combustion is responsible for over 97% of the world's bioenergy production[1]. However, ash related issues, such as deposition, corrosion and agglomeration (in fluidized bed) caused by alkali species from biofuel constitute a major impediment to a wider and more efficient utilization of biomass for power production [2-4]. An option to tackle these ash-related problems is the introduction of additives into boilers for transforming the harmful gaseous alkali compounds (e.g. KCl, KOH and K<sub>2</sub>SO<sub>4</sub>) into less corrosive ash species with a higher melting points [5]. Kaolin and coal fly ash have been proven to be effective in reacting with gaseous alkali species, and have received extensive research focus during the past decades [3, 6-10]. However, most of the previous studies on K-capture by solid additives were carried out in fixed-bed reactors or in thermogravimetric analysers, where the reaction conditions are significantly different from that in suspension fired boilers [8, 11, 12]. To the author's knowledge, study on alkali-capture by additives at suspension fired conditions is still rare except a series of study carried out by Wendt and co-workers [13, 14]. Detailed knowledge on the reaction between vaporized K-species and solid additives under suspension-fired conditions is still limited.

The objective of the present work, is to develop a method using an entrained flow reactor (EFR) to study the KCl capture reaction by different additives (kaolin and coal fly ash), under suspension-fired conditions. The impact of the type and amount of additives, reaction temperature, and particle size are investigated.

## 2. Experimental work

### 2.1. Experimental setup

The experiments were conducted in an entrained flow reactor (EFR) shown schematically in Figure 1. The EFR consists of a gas supply system, a slurry feeding system, a gas preheater, a 2 m long vertical reactor which is electrically heated by 7 heating elements, a bottom chamber and a particle and flue gas extraction system. The vertical reactor tube is made of silicon carbide (SiC) with an inner diameter of 0.08 m, and the maximum wall temperature is 1500 °C. At the conditions (1100 °C-1450 °C) investigated in this study, the gas residence time in the vertical reactor tube is 0.7 - 0.9 s.

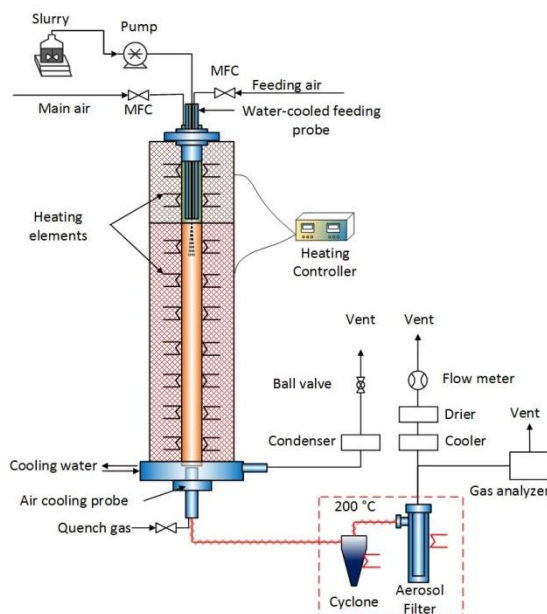


Figure 1. Schematic of entrained flow reactor (EFR)

Instead of feeding KCl (s) directly into the EFR [15], KCl and solid additives, including kaolin powder and coal fly ash, were mixed with deionized water, to make a homogeneous slurry which was magnetically stirred during the whole experiment. The slurry was consequently fed into the reactor by a peristaltic pump at a speed of about 3.2 g/min. The slurry was also added with 5 wt % ethanol which combusted in the reactor, forming CO<sub>2</sub>. The feeding rate of slurry can be monitored indirectly by measuring the CO<sub>2</sub> concentration in the flue gas. The slurry fed into the reactor was atomized at the outlet of the water-cooled feeding probe by a 30 NI/min feeding air. The atomized slurry droplets as well as KCl, were mixed with preheated main air (60 NI/min, 1000 °C-1200 °C), and subsequently evaporated. KCl and solid additives reacted in the vertical reactor tube. After reactions, the solid product samples were collected by a cyclone and a metal filter.

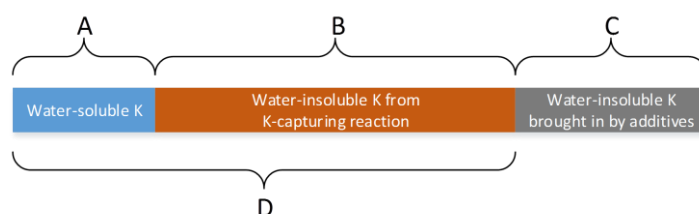


Figure 2. K-species in the reaction products

As shown in Figure 2, in the reaction products, K is present in both water-soluble (A) and water-insoluble phases. The water-insoluble K originates from two different sources: being formed by K-capturing reaction (B) or brought in by solid additives (C). The concentration of water-soluble K and water-insoluble K in the solid products was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis. The extent of reaction

between KCl and solid additives under different conditions was evaluated by the amount of water-insoluble K formed (B). In order to quantify the extent of K-capturing reaction, two parameters are defined: K-conversion fraction ( $X_K$ ) and K-capturing level ( $C_K$ ).  $X_K$  is the fraction of the injected KCl reacted with additives and transformed into water-insoluble K-aluminosilicate (%), while  $C_K$  is defined as the mass of K captured by 1 g solid additive through chemical reaction (g K/g additive). These two parameters are calculated as shown in Equation 1 and 2.

$$X_K = \frac{B}{D} \times 100\% \quad (1)$$

$$C_K = \frac{n_{KCl} M_K X_K}{m_{ad.}} \times 100\% \quad (2)$$

Where B is the amount of water-insoluble K formed by K-capturing reaction, and D is the amount of K from KCl which is fed into the reactor, as shown in Figure 2.  $n_{KCl}$  is the molar amount of KCl fed into the reactor;  $M_K$  is the molar mass of K (g/mol);  $m_{ad.}$  is the mass of solid additives fed into the reactor (g).

The quantification method utilized is based on the assumption that the collected solid samples are representative, which means that the collected and uncollected products have the same elemental composition. The representativeness of collected samples was checked by comparing the molar ratio of K/Al in collected products and reactants as shown below. If the ratio is close to 1, it implies that the collected products are representative.

$$\lambda = \frac{(K / Al)_{product}}{(K / Al)_{reactant}} \quad (3)$$

Additionally, the morphology of reacted solid products is studied with SEM (Scanning Electron Microscopy), in order to obtain an understanding of the mechanism of the reaction.

## 2.2 Experimental Matrix

Two types of solid additives were employed in this study: pulverized kaolin ( $D_{50} = 5.47 \mu\text{m}$ ), and, coal fly ash from Asnæsværket Power Plant, Denmark (ASV2). Al and Si are the major elements for both kaolin and coal fly ash utilized. The impact of different parameters, such as reaction temperature, solid additive particle size, and the molar ratio of K/(Al+Si) in reactants, were investigated in the present study. The mass ratio of K/(Al+Si) in the reactants was changed by adjusting the concentration of KCl in utilized slurries. The ASV2 coal fly ash, sieved to 0-32  $\mu\text{m}$  and 32-45  $\mu\text{m}$ , was utilized to investigate the influence of solid additive particle size on the reaction. Different reaction temperatures of 1100 °C, 1300 °C and 1450 °C, were studied with the matrix shown in Table 1.

Table 1. Experimental matrix

Additive	Temp./°C	K/(Al + Si) molar ratio	Gas residence time /s
<b>Kaolin</b>  <b>(<math>D_{50} = 5.47 \mu\text{m}</math>)</b>	1100	0.06	0.9
	1100	0.46	0.9
	1300	0.06	0.8
	1300	0.22	0.8

	1300	0.46	0.8
	1300	0.66	0.8
	1450	0.06	0.7
<b>Coal ash (0-32 <math>\mu\text{m}</math>)</b>	1100	0.06	0.9
	1300	0.06	0.8
	1300	0.48	0.8
	1450	0.06	0.7
<b>Coal ash (32-45 <math>\mu\text{m}</math>)</b>	1300	0.06	0.8
	1300	0.47	0.8

### 3. RESULTS AND DISCUSSION

#### 3.1. Representativeness of collected products

The representativeness of collected solid samples is examined by comparing the molar ratio of K/Al in collected products and that in reactants, with results of four tests shown in Figure 3. The results show that the molar ratio of K/Al in reactants is close to that of the collected solid samples, showing that the collected solid samples are representative, and the aforementioned quantifying method can be used for evaluating the reaction.

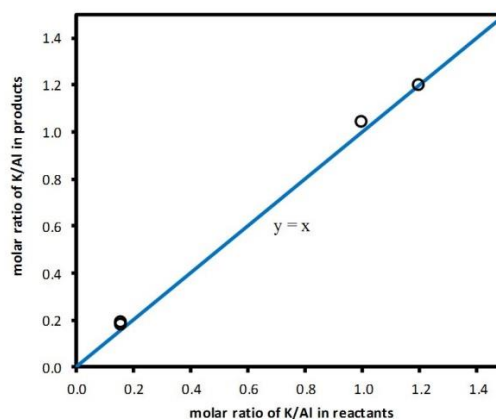


Figure 3. molar ratio of K/Al in reactant and product (all the four experiments are conducted at 1300 °C)

#### 3.2. Impact of molar ratio of K/(Al+Si) in reactants

For kaolin and coal fly ash, the active elements for capturing K are Al and Si. Therefore, the molar ratio of K/(Al+Si) indicates the relative amount of “active component” of additive to K-species in reactants. In addition, the K-capturing capability of different additives can be compared according to the value of  $C_K$ , at the same molar ratio of K/(Al+Si) in reactants.

Figure 4 shows that, for kaolin, with the increase of the molar ratio of K/(Al+Si) from 0.06 to 0.66 in the reactants, the conversion of KCl decreased from around 90 % to 30 %, implying more KCl stayed unreacted. For coal fly ash, it showed similar tendency as kaolin. Comparing to K-capture by coal fly ash in full-scale boilers where almost all K was transferred into water-insoluble species at molar ratio of K/(Al+Si) around 0.06 [9], the  $X_K$  in the EFR is

significantly lower. One possible reason is that the residence time in the EFR ( $< 1$  s) is obviously shorter than that in full-scale boilers.

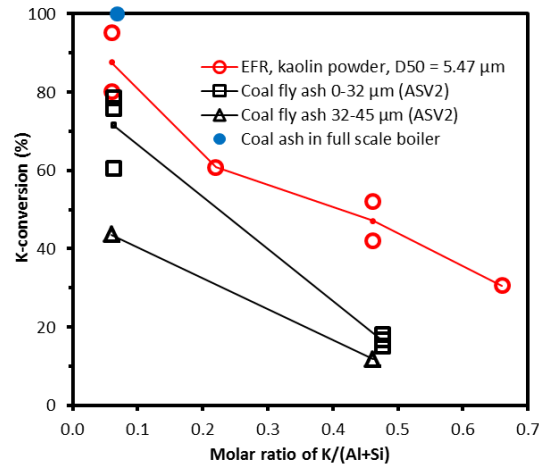


Figure 4.  $K$ -conversion ( $X_K$ ) using kaolin and coal fly ash as additive at different molar ratio of  $K/(Al+Si)$  in reactants (all experiments are conducted at 1300 °C)

### 3.3. Impact of temperature

SEM images in Figure 5 show that solid products collected from 1100 °C predominantly existed as flakes, while mainly spherical particles were collected from experiments at 1300 °C, implying that the melting point of the solid product is between 1100 °C and 1300 °C.

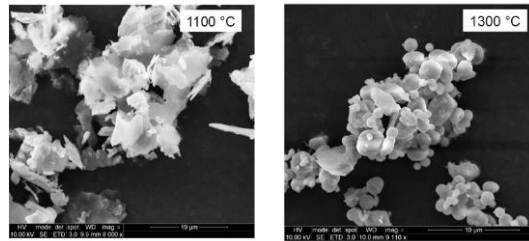


Figure 5: Reacted particles at different temperature (molar ratios of  $K/(Al+Si)$  in reactants are both 0.46)

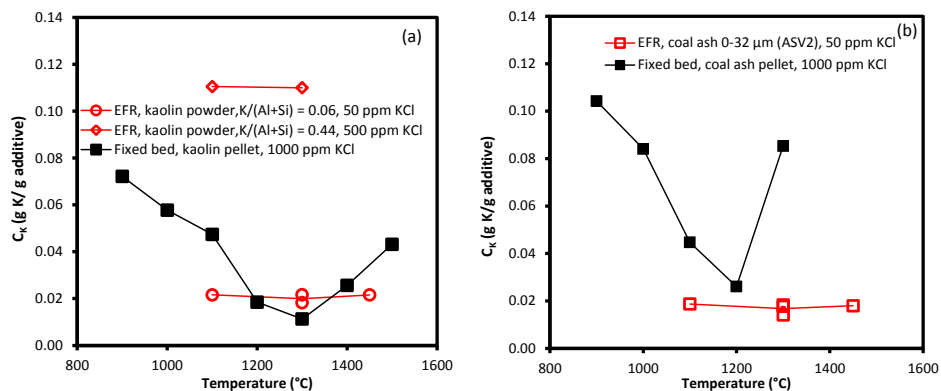


Figure 6. (a)  $K$ -capturing level ( $C_K$ ) by kaolin at different temperatures. Fixed bed reactor tests are conducted with kaolin pellets of diameter of 1.56 mm, residence time of 1 hour and KCl concentration of 1000 ppm [8]. (b)  $K$ -capturing level by coal fly ash with particle size  $< 32$  μm (ASV2) at different temperature. Fixed bed reactor tests are conducted with coal ash pellet of diameter of 1.50 mm, residence time of 1 hour and KCl concentration of 1000 ppm [8].

Figure 6 shows the  $K$ -capture level by kaolin and coal fly ash in EFR compared to results gained from fixed-bed reactor by Zheng [8]. It shows that changing reaction temperature from

1100 °C to 1450 °C does not pose significant impact on the extent of K-capture reaction in the EFR. However, in the fixed-bed reactor,  $C_K$  decreases with increasing temperature and reaches a minimum at 1300 °C, and then it increases again with increasing temperature. The K-capturing reaction in the fixed bed is controlled by internal diffusion in additive pellets, and the transformation of metakaolin to less active mullite as well as sintering of the additive pellets below 1300 °C is responsible for the decreasing trend of  $C_K$  in the fixed bed. The formation of a molten phase, at temperatures higher than 1300 °C, contributes for the increasing of  $C_K$  [8]. However, in the EFR, instead of additive pellets, kaolin and coal fly ash particles are dispersed in the flue gas, and more than 70 wt % kaolin particles are smaller than 10 µm according to the particle size distribution (PSD) analysis. Therefore, the K-capturing reaction in EFR is probably kinetic-controlled or equilibrium controlled. However, further investigations are required to improve the understanding of the controlling mechanisms.

Another interesting result shown in Figure 6 is that  $C_K$  in the EFR is higher or similar, compared to that in fixed-bed, although the residence time in the EFR is much shorter, and the concentration of KCl is much lower. At 500 ppm KCl in the EFR, the  $C_K$  of kaolin is around 0.11 g K/g additive, compared to less than 0.05 g K/g additive in the fixed-bed reactor at 1000 ppm KCl. At 50 ppm KCl in the EFR, kaolin can reach similar K-capturing levels with that in the fixed-bed reactor at 1000 ppm KCl. The results imply that dispersed kaolin particles in flue gas can capture gaseous KCl much more efficiently than additives in the form of pellets which was widely employed in previous studies [6, 11, 16]. However, the  $C_K$  in EFR is still lower than the theoretical maximum value (0.3 g K/g kaolin) which is calculated according to the following reaction R1 and R2.



## 4. CONCLUSIONS

A method of studying the reaction of capturing gaseous K-species, by solid additives under suspension-fired conditions was developed, using an entrained flow reactor (EFR). The method makes it possible to investigate the influence of reaction temperature, residence time, additive particle size and, alkali concentration on the K-capturing reaction by different additives. Kaolin and coal fly ash, were employed in the present study.

The results showed that under suspension-fired conditions, kaolin powder and coal fly ash can effectively capture gaseous KCl in flue gas. The conversion of KCl into K-aluminosilicate ( $X_K$ ) decreases with increasing molar ratio of K/(Al+Si) in reactants. When changing reaction temperature from 1100 °C to 1450 °C in the EFR, the K-capturing level did not change obviously which differs from that observed in fixed-bed reactors. The results indicate a different reaction controlling mechanism for K-capturing reaction by dispersed solid additives. A detailed explanation of these observations needs further experimental investigation and analysis.

## 5. FUTURE WORK

The developed method using the EFR in this study will be used for future systematic quantitative investigation of different solid additives. The experimental data gained in this study will be used for developing a mathematical model describing the K-species capture and providing recommendations for optimal use of the additives in suspension-fired full-scale boilers.

## 6. ACKNOWLEDGEMENTS

This work is part of the project 'Flexible use of Biomass on PF fired power plants' funded by Energinet.dk through the ForskEL programme, DONG Energy and DTU.

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